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IRREVERSIBILITY OF THE ALUMINUM ELECTRODE IN BASIC
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FRANK J. SEILER RESEARCH LABORATORY

**IRREVERSIBILITY OF THE
ALUMINUM ELECTRODE
IN BASIC ROOM-TEMPERATURE
CHLOROALUMINATE MOLTEN SALTS**

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This report has been reviewed by the Commander and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.


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| 19. ABSTRACT (Continue on reverse if necessary and identify by block number) The irreversibility of the aluminum electrode in basic room temperature chloroaluminate melts has been attributed to an apparent kinetic barrier to reduction of the stable tetrachloroaluminate ion. Six approaches were identified which might lead to promoting reduction of Al from basic melts or at least provide some understanding of whether and how this barrier might be overcome. Our results showed that reduction of Al in basic $\text{HfCl}/\text{AlCl}_3$ melts was not promoted by (1) elevated temperatures (up to 181°C), (2) substitution of mixed haloaluminates, $\text{AlCl}_x\text{Br}_{4-x}^-$ for AlCl_4^- , or (3) introducing LiCl , BF_3 , and MgCl_2 into melts. (4) Cyclic voltammetry of melts dissolved in THF did not provide any evidence of AlCl_4^- reduction. (5) Melts formed from dimethylethylethoxymethyl ammonium chloride ($\text{N}_{211} 102\text{Cl}$) and AlCl_3 did have a cathodic limit that was about 0.6 V more negative in basic melt than that for $\text{HfCl}/\text{AlCl}_3$. However, no AlCl_4^- reduction was observed in basic $\text{N}_{211} 102\text{Cl}/\text{AlCl}_3$ melts. Finally, (6) some preliminary semi-empirical molecular orbital calculations gave results which indicate that further refinement of a (SEE REVERSE) | | | | | | | | | | | | |
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cont'd model for the AlCl_3 reduction process is worth pursuing. A mechanism for the electrode process at equilibrium is proposed which is consistent with a true thermodynamic equilibrium and the absence of Al deposition at potentials cathodic of the rest potential.

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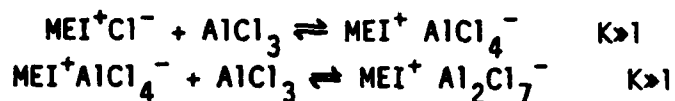
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Introduction

Mixtures of 1-methyl-3-ethylimidazolium chloride (MEICl) and AlCl_3 form salts which are liquid at and well below room temperature (1,2). The anionic species present in the melts with $N < 0.67$ ($N = \text{mol AlCl}_3 / (\text{mol AlCl}_3 + \text{mol MEICl})$) are dictated by the following reactions:



If the amount of AlCl_3 used in preparing the melt gives $N < 0.5$, Cl^- and AlCl_4^- are the anions present, and such melts are basic since Cl^- acts as a Lewis base. For $N > 0.5$, AlCl_4^- and Al_2Cl_7^- are present and such melts are acidic since Al_2Cl_7^- acts as a Lewis acid. The dependence of anion fractions on N is shown in Fig. 1. Above $N=0.67$, other species, including Al_2Cl_6 and $\text{Al}_3\text{Cl}_{10}^-$ are also present, but these melts are not liquid at room temperature. Also, mixtures with $N < 0.33$ are not room temperature melts.

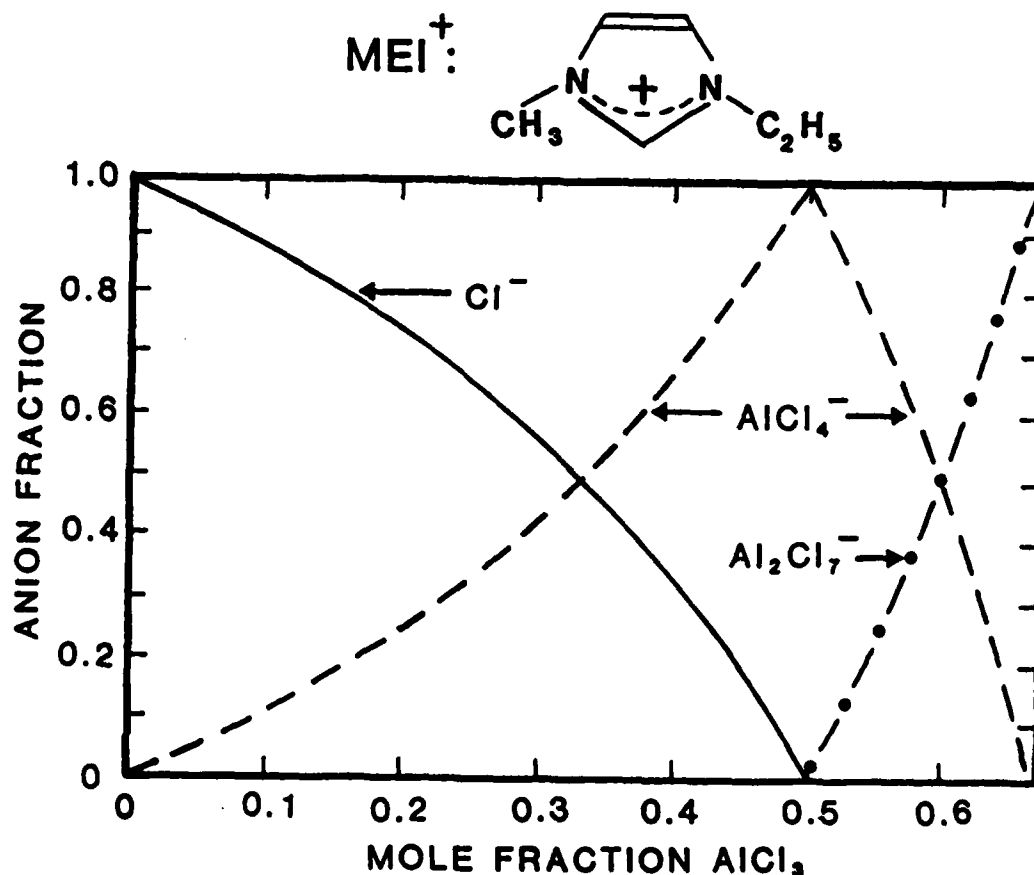


Fig 1. Anion fraction in MEICl/ AlCl_3 melts as a function of mole fraction, N , of AlCl_3 .

Aluminum stripping and deposition occur reversibly in acidic melts (3), but only oxidation of Al has been observed to occur in basic room temperature melts by the reaction,



This is not the case in high temperature inorganic systems in which deposition of Al has been reported from basic KCl-NaCl-AlCl₃ melts (4). Thus raising the temperature of basic MEICl/AlCl₃ melts was suggested as a way to induce Al deposition. Other approaches involve attempts to reduce the stability of the tetrahedral aluminate structure. This can be tested by using mixed tetrahaloaluminates, which are readily formed by adding AlCl₃ and AlBr₃ to MEICl (5). Addition of the salts, LiCl and MgCl₂, and BF₃ might also destabilize the AlCl₄⁻ ion by its interaction with the Li⁺ or Mg²⁺ even if they exist primarily as the chloro complexes LiCl₂⁻ and MgCl₄²⁻, as has been suggested (6). Another approach involved extending the cathodic limit by using solutions of basic melts in tetrahydrofuran (THF). The cathodic limit in neat basic melts is MEI⁺ reduction which occurs at ~-2.0 V vs an Al/N-0.60 melt. Dilute solutions of basic melts in THF should allow observation of AlCl₄⁻ reduction if it occurs at potentials positive of the THF reduction. Another effort to extend the cathodic limit involves use of an organic chloride with a different cation, dimethylethylethoxymethyl ammonium chloride (N₂₁₁ 102Cl). Finally, semi-empirical molecular orbital calculations using the MNDO technique in the MOPAC program (7) were used to study the process of AlCl₄⁻ reduction theoretically.

In summary then, the following approaches were used to investigate the barrier to Al reduction in basic melts.

1. Elevated temperatures.
2. Mixed haloaluminates.
3. Addition of salts with strongly "interacting" cations.
4. Extension of cathodic limit using THF.
5. New organic cations.
6. Theoretical calculations.

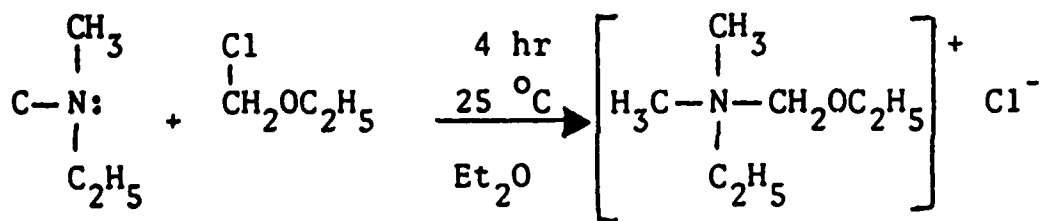
Experimental

MEICl was prepared as described previously (8) except that product was in some cases recrystallized from acetonitrile alone instead of from

acetonitrile/ethyl acetate. AlCl_3 and AlBr_3 were purified by distillation. LiCl (Mallinckrodt Analytical Reagent) was dried for 15 hours at 120°C and then placed in a vacuum dessicator for two hours. Purified MgCl_2 was obtained in sealed containers from the laboratory of the Norwegian Technical Institute at Trondheim, Norway. BF_3 (Matheson lecture bottle) was added to the melt in a gas-handling system in which pressures were monitored with MKS Baratron capacitance manometers. Concentrations of Mg, Li, and B in melts were measured using an ARL Inductively Coupled Plasma Atomic Emission Spectrometer. Preparations of melts, including those with salts added, were done either under vacuum or in a helium-filled dry box with $\text{O}_2/\text{H}_2\text{O}$ at 10 ppm or less.

THF, used as solvent in melt solutions, was dried by distillation from sodium benzophenone. Tetrabutylammonium perchlorate (at 0.1 M) was used as a supporting electrolyte.

The $\text{N}_{211} \text{ } ^{102}\text{Cl}$ was prepared as shown below:



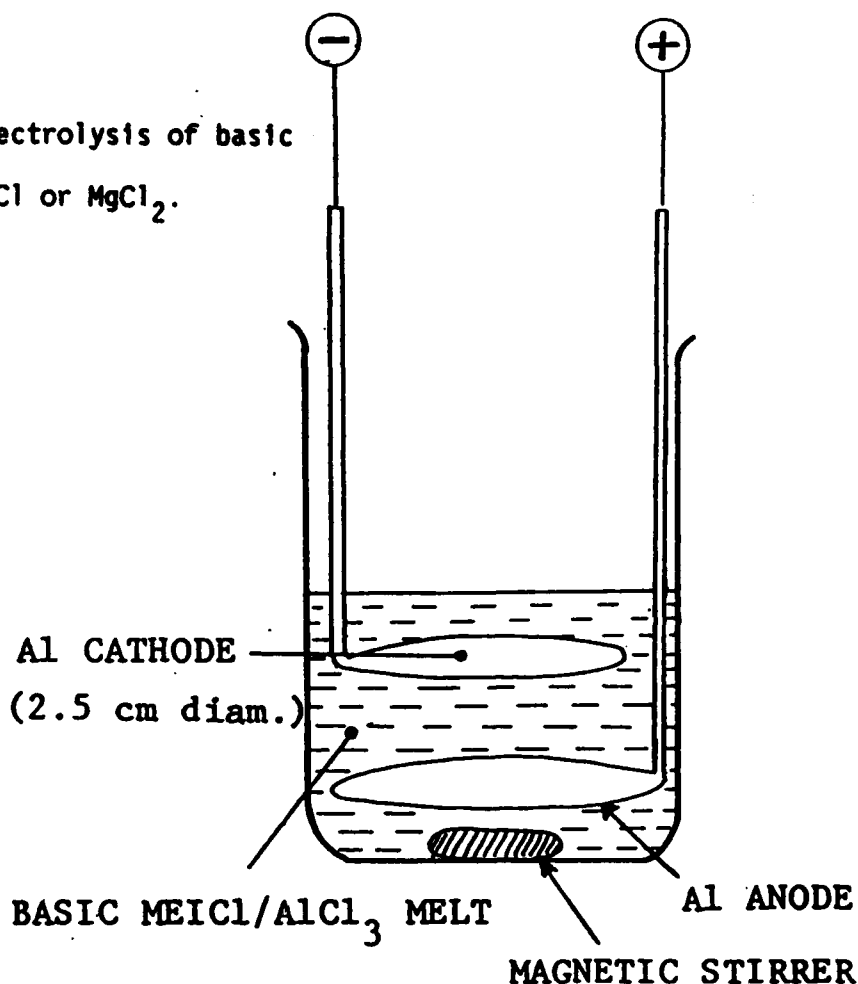
- Add amine dropwise to chloroether
- Remove solvent via cannula
- Dry in vacuum
- No further purification required (90% yield)

Cyclic voltammograms (CV's) were obtained using a PAR 173 Potentiostat, a PAR 175 Programmer and an X,Y-recorder. A variety of working electrodes were used, but a molybdenum counter electrode was used in all cases. The reference electrode was either an $\text{Al}/(\text{N}=0.6 \text{ MEICl}-\text{AlCl}_3 \text{ melt})$; an Ag/AgNO_3 (acetonitrile) for experiments in acetonitrile solutions; or Ag/AgNO_3 ($\text{N}=0.4 \text{ N}_{211} \text{ } ^{102}\text{Cl}/\text{AlCl}_3 \text{ melt}$). In experiments with elevated temperatures, the cells were placed in an electrical furnace with a temperature controller that gave $\pm 1^\circ\text{C}$ accuracy. All CV's were done in the He-filled dry box.

LiCl and MgCl_2 were added to basic melts in saturated concentrations. These melts were then subjected to electrolysis between two Al electrodes.

The electrolysis experiments were done in the dry box at a constant current in a cell as shown in Fig. 2, with the current and potential monitored using a PAR 173 Potentiostat. The Al cathode, which was first abraded with carborundum paper and rinsed with acetonitrile, was weighed before and after passage of a measured charge (monitored with a par Model 179 Digital Coulometer).

Fig 2. Cell used for electrolysis of basic melts saturated with LiCl or MgCl₂.



Results

1. Elevated temperatures. Cyclic voltammograms (CV's) of Al in an N=0.40 MEICl/AlCl₃ melt at various temperatures are shown in Fig. 3. As the temperature is increased, the rest potential shifts to more negative values and the cathodic limit, reduction of MEI⁺, occurs at more positive potentials. However, there is no indication that deposition of Al occurs at the higher temperatures. A similar result was obtained when a Pt working electrode was used, except that in those CV's, the anodic limit was oxidation of Cl⁻.

2. Mixed haloaluminates. A mixed haloaluminate melt was prepared with mole ratio of MEICl:AlCl₃:AlBr₃ of 20:9:9. This gives a slightly basic melt

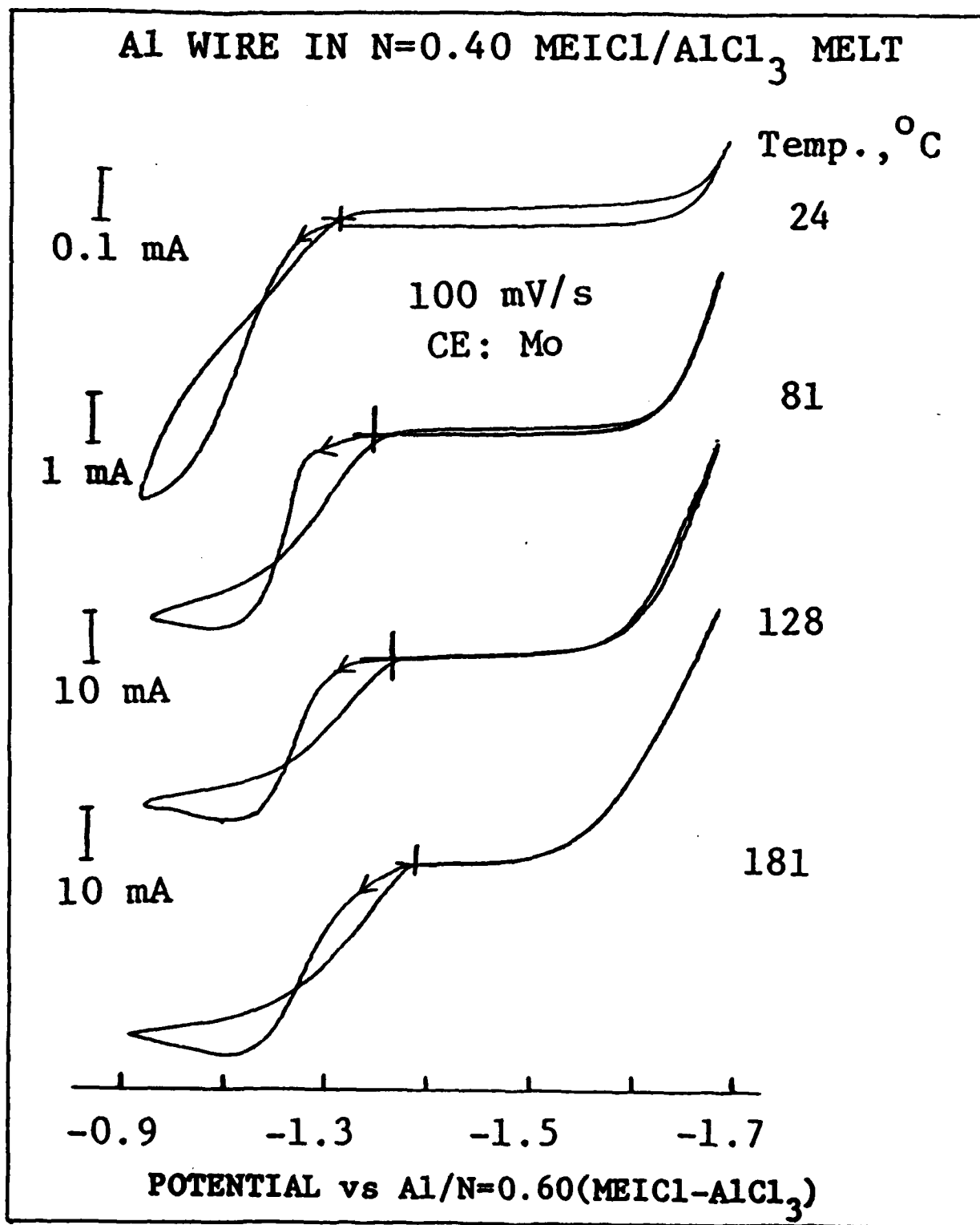


Fig 3. Cyclic voltammograms of Al in MEICl/AI₃ melts with N = 0.40 at various temperatures.

with all $\text{AlBr}_x\text{Cl}_{4-x}^-$ species present as has been observed with ^{27}Al NMR (5). Fig. 4 shows the CV's obtained at a Pt working electrode at various temperatures. The more complex anodic limit involving oxidation of both Cl^- and Br^- is evident. However, again there is no indication of Al deposition. The cathodic limit is MEI^+ reduction and no oxidation wave associated with stripping of deposited Al, which would occur at ~ -1.3 V, is detected.

3. Addition of salts with strongly interacting cations. BF_3 addition to an $N=0.33$ $\text{MEICl}/\text{AlCl}_3$ melt was controlled by introducing fixed pressures of BF_3 into the flask containing the melt evacuated to 10^{-5} torr. The BF_3 was readily dissolved into the melt until the BF_3 concentration was 2.66 mol/L. This corresponds to an amount of BF_3 equal to the Cl^- present in the melt and strongly suggests that the complex BF_3Cl^- is formed and that after all the available Cl^- is used, no further BF_3 can be dissolved. The CV's with various concentrations of BF_3 are shown in Fig. 5. The CV's show no evidence of Al deposition or electrochemical activity of the BF_3Cl^- .

The results of the electrolysis experiments on $N=0.40$ melts saturated with MgCl_2 and LiCl are shown in Table 1.

Table 1

ELECTROLYSIS OF $N=0.40$ MELTS SATURATED WITH LiCl AND MgCl_2

| | | <u>LiCl</u> | <u>MgCl_2</u> |
|---|---------|---------------------------------|-----------------------------------|
| $\left[\frac{\text{mol } \text{MgCl}_x}{\text{mol } \text{MEI}^+} \right]$ | initial | 0.095 | 0.109 |
| | final | 0.093 | 0.110 |
| Charge, C | | 212 | 98 |
| Potential, V | | 1.5-2.0 | 1.0 |
| Current, mA | | 3.5 | 2.0 |
| Calculated Δ Mass Al Cathode ($3e^- + \text{AlCl}_4^- \rightarrow \text{Al} + 4\text{Cl}^-$) | | 0.0198g | 0.0091 |
| $\left[\begin{array}{l} \text{Mass Al Cathode} \\ (\pm 0.0002\text{g}) \end{array} \right]$ | initial | 0.4216 | 0.7008 |
| | final | 0.4217 | 0.7010 |

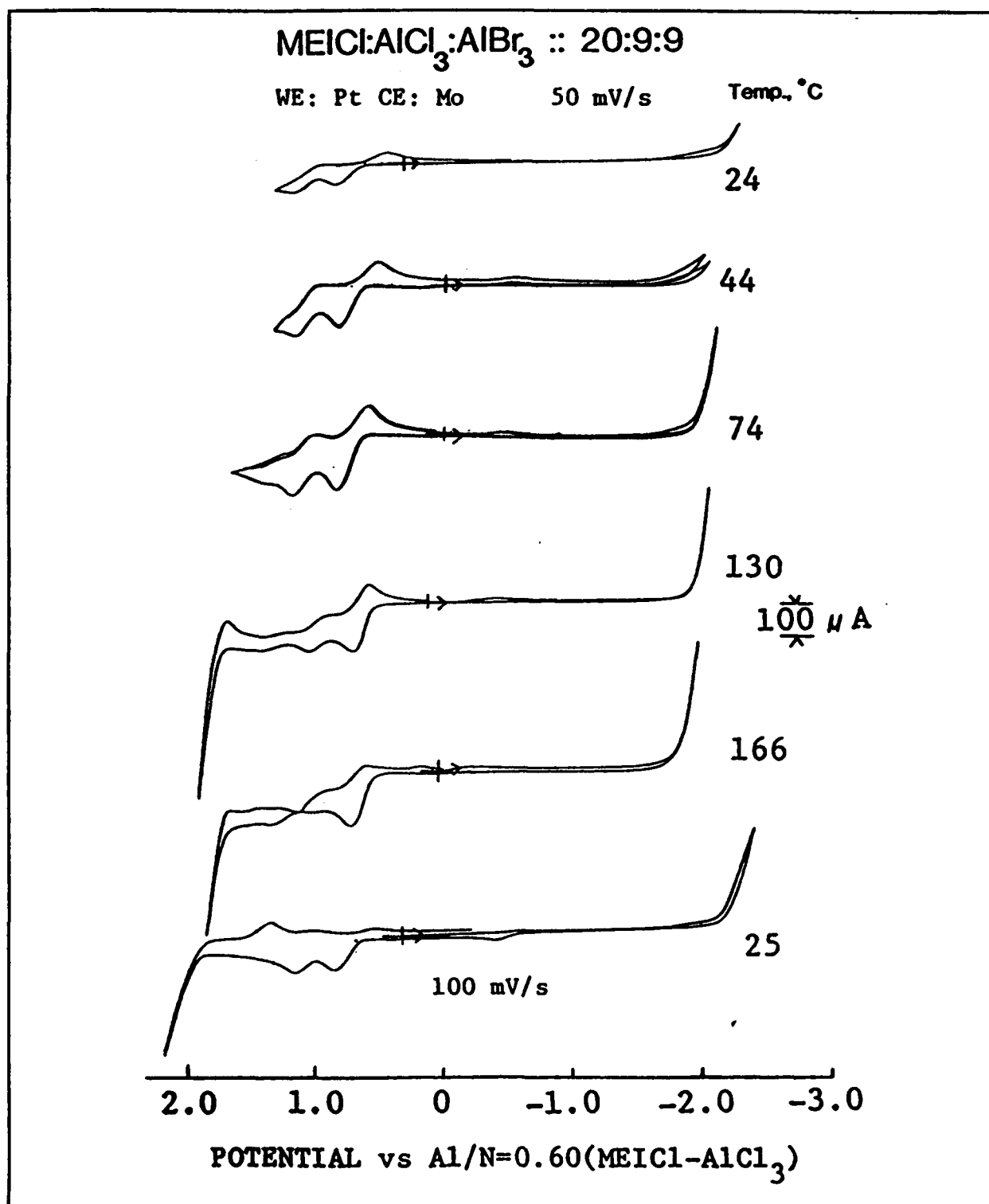


Fig 4. Cyclic voltammograms of basic $\text{MEICl}/\text{AlCl}_3 + \text{AlBr}_3$ melts on Pt electrode at various temperatures.

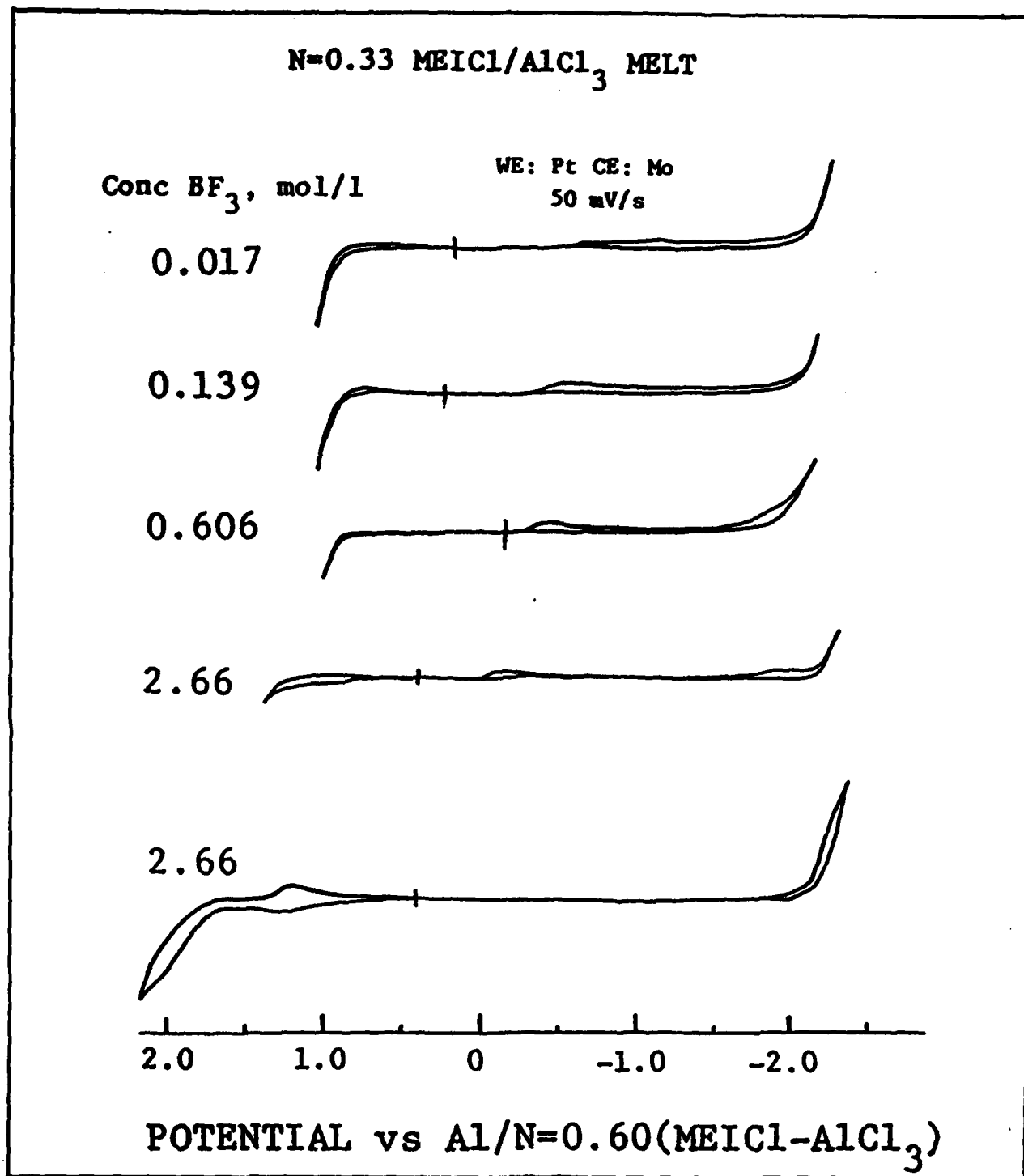


Fig 5. Cyclic voltammograms of $N = 0.33 \text{ MEICl/AlCl}_3$ melts with various concentrations of BF_3 on Pt electrode. $T = 28^\circ\text{C}$.

The intent of the electrolysis experiments was to determine if Al was being deposited but at rates too low to be detected by CV's. Within the experimental error limits, no changes in the mass of the Al cathode was observed for either the LiCl or MgCl₂ solutions. It is interesting to note that both salts are soluble to about the same extent, i.e., 11% mol fraction in basic melts as measured by the ICP atomic emission spectroscopy on the melts before and after the electrolysis.

4. Extension of cathodic limit using THF. Fig. 6 shows the CV's of solutions of melts in THF using a Pt working electrode. The reduction wave for MEI⁺ is within the electrochemical window of the THF, and it appears to be the only reduction process occurring before the cathodic limit is reached. No oxidation wave is observed in the potential range in which we would expect Al oxidation to occur (-1 to 0 V vs Ag/AgNO₃). The oxidation at ~0.5 V is most likely due to products of the MEI⁺ reduction. This oxidation wave is observed in increasing intensity in basic melts as MEI⁺ reduction is carried out at increasingly negative potentials. The peak at +2 V in the CV for the 0.003 M (N=0.33) solution is probably due to AlCl₄⁻ oxidation to Cl₂.

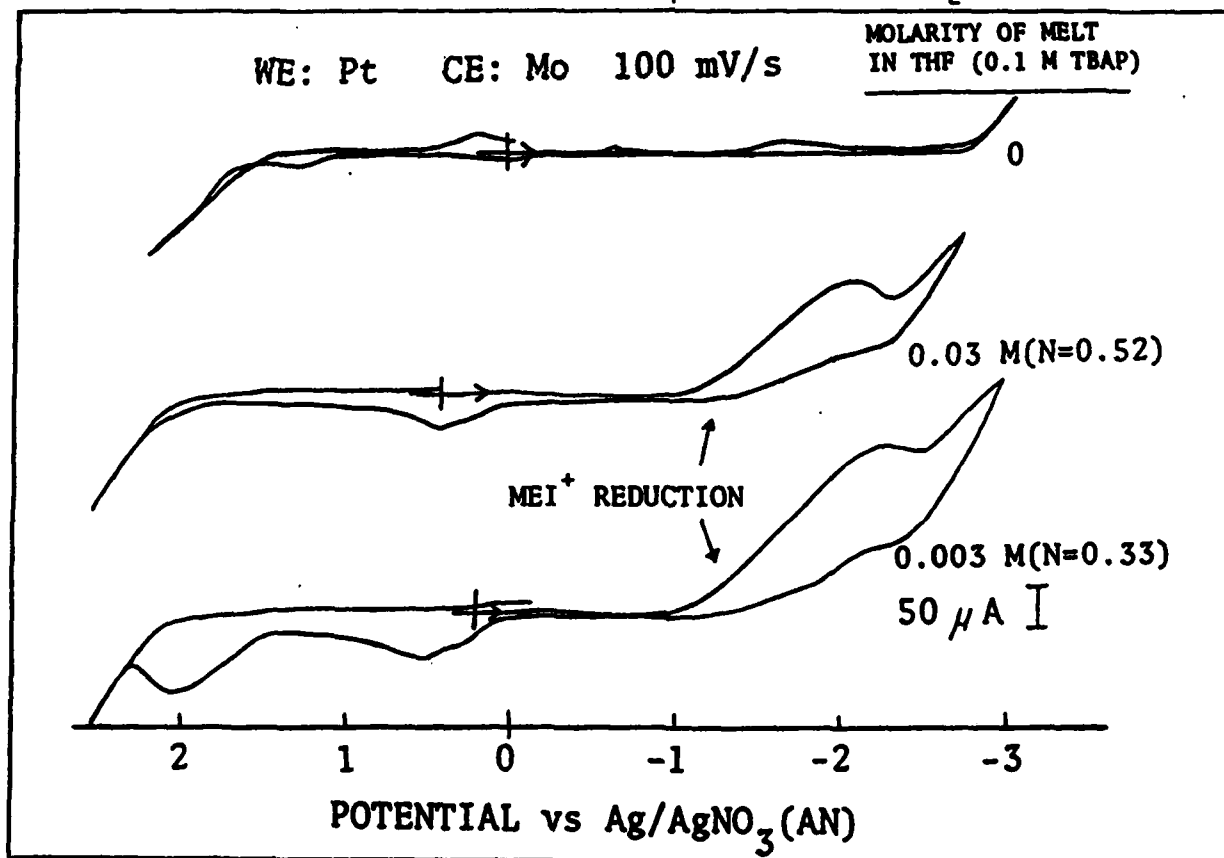


Fig 6. Cyclic voltammograms of tetrahydrofuran solutions of melts on a Pt electrode with tetrabutylammonium perchlorate supporting electrolyte at 0.1M.

5. New organic cations. Dimethylethylethoxymethyl ammonium chloride ($N_{211} 102 Cl$) was selected on the basis of its similarity to a series of compounds reported by Angell (9). These are generally expected to form low-melting salts when mixed with $AlCl_3$. Furthermore, MNDO calculations on this type of cation indicated it should have a more negative reduction potential than MEI^+ (10). The $N_{211} 102 Cl$ did in fact form room temperature melts when added to $AlCl_3$. However, only basic melts were chemically stable. Acidic melts underwent a reaction in which C_2H_5Cl was released, as determined by GC/MS analysis of the gas evolved during decomposition. CV's of $N_{211} 102 Cl/AlCl_3$ melts with $N=0.4$ for Pt, Al, and Cd electrodes are shown in Fig. 7. Corresponding CV's for $MEICl/AlCl_3$ melts with $N=0.4$ are shown for comparison.

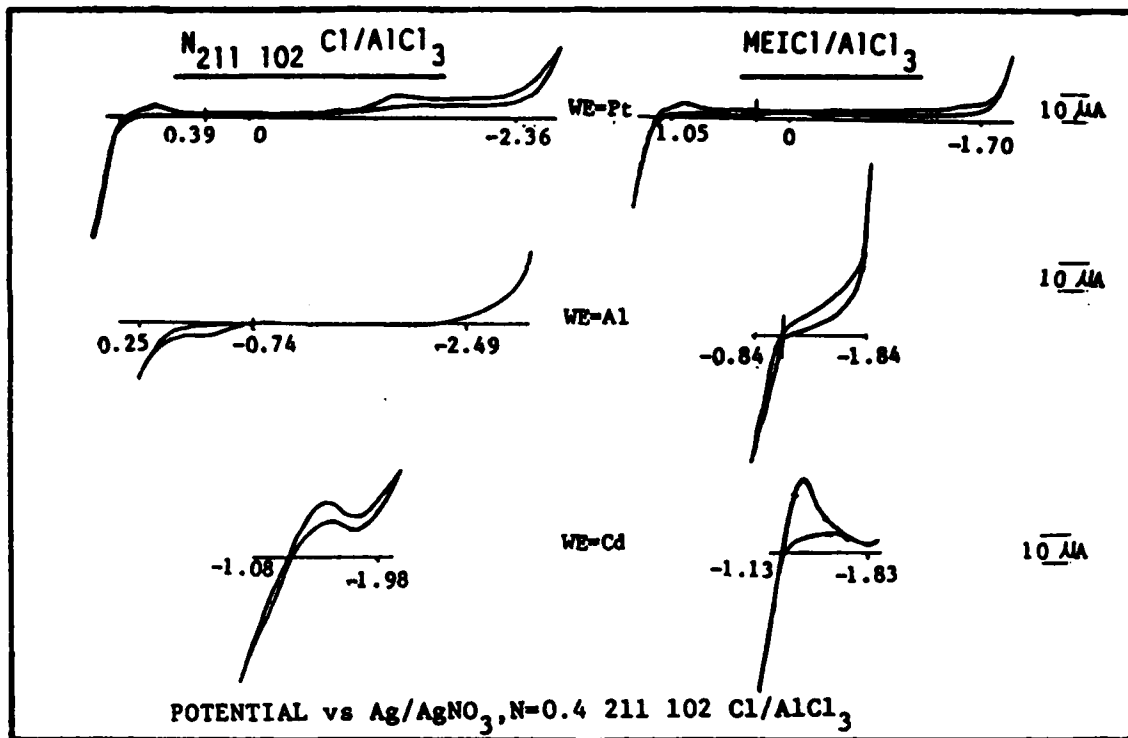


Fig 7. Cyclic voltammograms of Pt, Al, and Cl electrodes in $N = 0.4$ melts of $MEICl/AlCl_3$ and $N_{211} 102 Cl/AlCl_3$ melts. Potentials measured as $Ag/AgNO_3$ ($N = 0.4$ $N_{211} 102 Cl/AlCl_3$ melt). Scan rates at 100 mV/s.

A significant increase in the electrochemical window due to the lower reduction potential of the $N_{211} 102^+$ cation is observed. Al oxidation occurs in the basic $N_{211} 102 Cl$ melt, though not as readily as in the $MEICl$ melt. And

more importantly, no indication of Al deposition occurs as the cathodic limit on both Al and Pt appears to be irreversible $N_{211} 102^+$ reduction. As in MEICl melts, Cd does form a reversible electrode in basic $N_{211} 102Cl$ melt. A more complete description of the physical and electrochemical properties of the $N_{211} 102Cl/AlCl_3$ melt system is in preparation.

6. Theoretical calculations. The MNDO technique has been used successfully in studies of melt properties (11). However, the question of what the barrier is to $AlCl_4^-$ reduction is a more difficult problem because it involves electron transfer and bond rupture at a solid-liquid interface. The reduction of $AlCl_4^-$ has been reported (4) at 975K in equimolar NaCl - KCl melts with $[AlCl_3]$ at $5 \times 10^{-5} - 5 \times 10^{-4} \text{ mol cm}^{-3}$. The deposition of Al was found to be diffusion controlled and to involve a fast charge transfer, with the primary transfer of a single charge as the rate-determining step. The rate constant was found from voltammetric methods to be 0.2 cm s^{-1} .

In this work, no attempt was made to reproduce experimental results. Rather, we wanted to probe the usefulness of MNDO in studies of the microscopic aspects of the charge transfer by constructing some simplified models. Two possible initial steps in the electron transfer process were compared in terms of their heats of reaction. The first model, shown in Fig. 8, involves $AlCl_4^-$ at a negatively charged rigid cluster of Al atoms in the form $Al_4H_6^-$ (representing a crude approximation of an electrode surface). The Al's are "capped" with H atoms, and the bonds between the Al atoms are modelled as covalent rather than metallic or "near-metallic." Each of the curves shown is obtained for a fixed distance between the central Al's of the $AlCl_4^-$ and $Al_4H_6^-$. The heat of formation is calculated for the optimized geometry obtained at a given Al-Cl bond length (where the Cl is the "leaving group" in the $AlCl_4^-$). Then the Al-Cl distance is fixed at a larger value and the next heat of formation for the optimized geometry is calculated. This is continued until Al-Cl is at 5 Å, which completes simulation of the process of breaking the Al-Cl bond to form a Cl^- and the $(AlCl_3-Al_4H_6)^-$ complex. With the Al-Al distance fixed at 3 Å, this process involves passage through a 39 kcal/mol barrier. During the process, the charge on the Al_4H_6 decreases from -1 to -0.64, and the $AlCl_3$ takes up the transferred charge. While it is not hard to visualize the primary step in $AlCl_4^-$ reduction occurring by such a mechanism, the model clearly has many limitations which we are trying to overcome. These problems include lack of any potential gradient, lack of

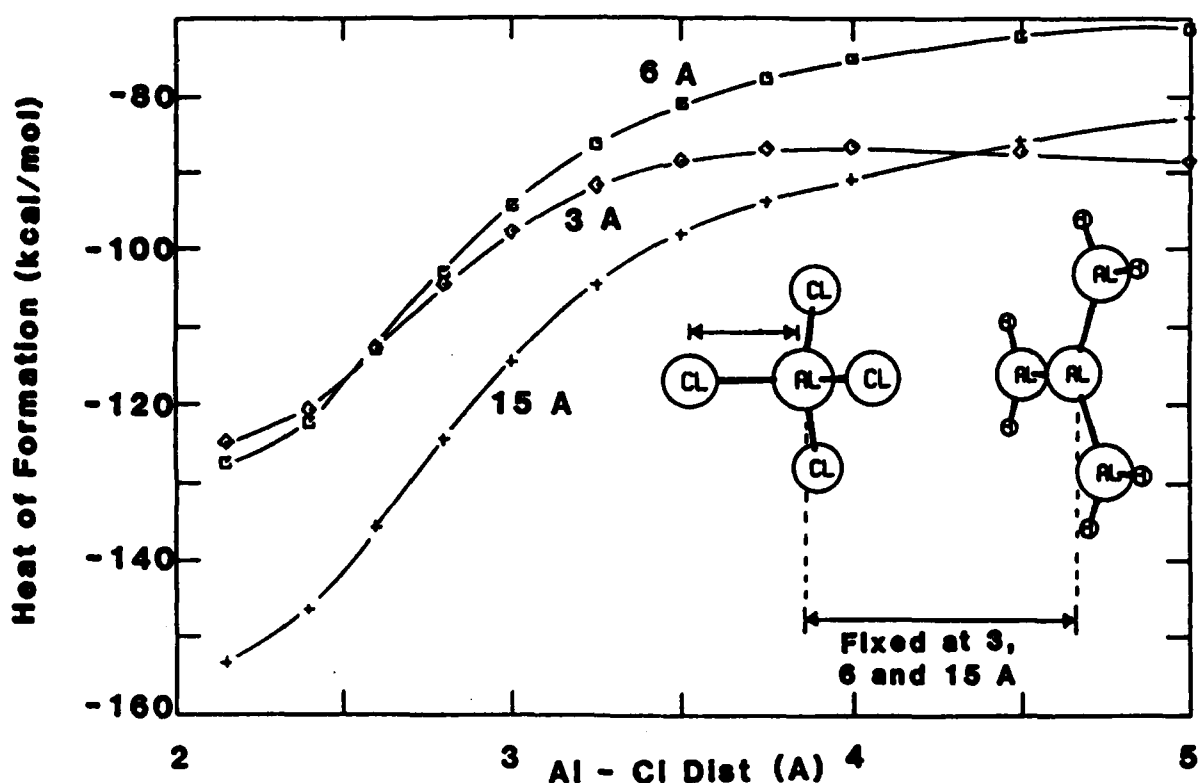
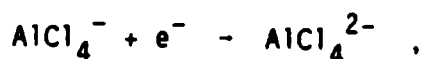


Fig 8. MNDO calculated heats of formation for the approach of AlCl_4^- to a negatively charged cluster of Al atoms with rupture of the Al-Cl bond as the reaction coordinate.

counterions, and an "electrode surface" whose energy changes. Nevertheless, this result can be compared to the change in enthalpy for the process,



which was calculated to be 66 kcal/mol. So at least these preliminary results are consistent with the intuitive expectation that it is more likely that some change in the AlCl_4^- structure occurs before electron transfer occurs than that a divalent AlCl_4^{2-} is formed.

Discussion and Conclusions

Our results showed that reduction of Al in basic $\text{MEICl}/\text{AlCl}_3$ melts was not promoted by

1. elevated temperatures (up to 181°C),
2. substitution of mixed haloaluminates, $\text{AlCl}_x\text{Br}_{4-x}^-$ for AlCl_4^- , or
3. introducing LiCl , BF_3 , and MgCl_2 into melts.

Cyclic voltammetry of melts dissolved in THF did not provide any evidence of AlCl_4^- reduction at potentials more negative than that for MEI^+ reduction. The melt formed from $\text{N}_{211} \text{102Cl}$ and AlCl_3 did have a cathodic limit that was about 0.6 V more negative in basic melt than that for $\text{MEICl}/\text{AlCl}_3$. However, no AlCl_4^- reduction was observed in basic $\text{N}_{211} \text{102Cl}/\text{AlCl}_3$ melts. Finally some preliminary semi-empirical molecular orbital calculations gave results which indicate that further refinement of a model for the AlCl_4^- reduction process is worth pursuing.

An important issue that this work has focussed our attention on is the nature of the reduction and oxidation reactions which occur when an Al electrode is placed in a basic $\text{MEICl}/\text{AlCl}_3$ melt and its potential is measured. While there appears to be no reason to doubt that the oxidation reaction is



the fact that the reverse reaction is not observed raises the questions: Does the measured rest potential correspond to the true equilibrium potential for this reaction? Can the absence of a reduction wave be accounted for by a kinetic barrier only?

Other possible descriptions of this electrode process include that this is a mixed potential in which Al is being oxidized by MEI^+ analogous to the situation observed in basic butylpyridinium chloride (BPC) - AlCl_3 melts (12). This is unlikely since the corrosion rate for Al in basic MEICl melts is quite low, $\sim 0.2 \mu\text{A}/\text{cm}^2$ (13), and unlike the case of BPC melts, stable and reproducible potentials are obtained.

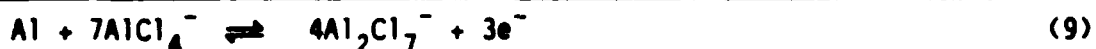
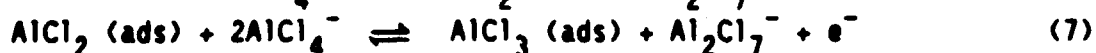
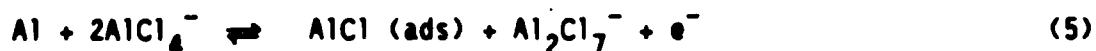
It is also possible that reduction of protonic impurities in the melt assumes control of the potential. While this suggestion merits further investigation, it also seems unlikely since the rest potential is quite reproducible for various melts in which protonic impurity concentrations are very likely to vary. Also, the potential is a smooth function of basic melt composition in potentiometric titrations (14).

The question then remains of how a sufficiently high exchange current for the reverse process, AlCl_4^- reduction to Al, to control the rest potential is possible. A mechanism for the equilibrium reactions which is consistent with a controlling exchange current and the observed irreversibility is:



where $\text{AlCl}_3 (\text{ads})$ is a species adsorbed on the electrode surface. None of the steps would be expected to be kinetically slow. However, when the reaction is driven to the left by a cathodic potential, the very large equilibrium constant for step (3) keeps the "reaction intermediate," Al_2Cl_7^- , at concentrations which are too low to sustain a reduction current. An important aspect of this mechanism is that the net equation, step (4), would be the equilibrium which determines the potential of an Al electrode in basic melt.

The $\text{AlCl}_3 (\text{ads})$ species could also be fit into a mechanism for the reversible Al electrode in acidic chloroaluminate melts, as shown below:



Here we show the stepwise buildup of the $\text{AlCl}_3 (\text{ads})$ species implicit in step (1) of the proposed mechanism in basic melt. In the acidic melt mechanism, the electroactive species are present in sufficient concentration to support both oxidation and reduction.

We are currently trying by theoretical and experimental methods to determine whether steps (1) - (3) are in fact the mechanism by which equilibrium is established at an Al electrode in basic melts.

References

1. A. A. Fannin, Jr., L. A. King, J. A. Levisky, and J. S. Wilkes, J. Phys. Chem., **88**, 2609 (1984).
2. A. A. Fannin, Jr., D. A. Floreani, L. A. King, J. S. Landers, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes, and J. S. Williams, J. Phys. Chem., **88**, 2614 (1984).
3. J. J. Auborn and Y. L. Barberio, J. Electrochem. Soc., **132**, 598 (1985).
4. Y. J. Zhang, A. Björgum, U. Erikson, R. Tunold, and R. Ødegard, J. Electroanal. Chem., **210**, 127-136 (1986).
5. From as yet unpublished NMR data obtained in our laboratory.
6. T. B. Scheffler, H. E. Klei, G. F. Reynolds, and J. S. Wilkes, "Preliminary Studies of New Molten Salt Systems Based on 1-Methyl-3-Ethylimidazolium Chloride Salts Other than Aluminum Chloride," 168th National Meeting of the Electrochemical Society, Las Vegas, NV, 13-18 Oct 85.
7. J. J. P. Stewart, Quantum Chem. Prog. Exchange Bull., **6**, 91 (1986); QCPE Program 455, Version 3.1.
8. FJSRL Group, FJSRL-TM-83-0016, June 1983, The Frank J. Sella Research Laboratory, USAF Academy, Colorado Springs, CO.
9. E. Cooper and A. Angell, Solid State Ionics, **9-10 (Pt 1)**, 616 (1983).
10. J. S. Wilkes and C. L. Hussey, FJSRL-TR-82-0002, January 1982, The Frank J. Sella Research Laboratory, USAF Academy, Colorado Springs, CO.
11. L. P. Davis, C. J. Dymek, Jr., J. J. P. Stewart, H. Clark, and M. J. Lauderdale, J. Am. Chem. Soc., **107 (18)**, 5041 (1985).
12. R. J. Gale and R. A. Osteryoung, J. Electrochem. Soc., **127**, 2167 (1980).

13. C. J. Dymek, Jr., J. L. Williams, D. J. Groeger, and J. J. Auborn, J. Electrochem. Soc., 131 (12), 2887 (1984).
14. C. L. Hussey, T. B. Scheffler, J. S. Wilkes, and A. A. Fannin, Jr., J. Electrochem. Soc., 133 (7), 1389 (1986).
15. J. G. Eberhart, FJSRL-TR-84-0004, August 1984, The Frank J. Sellar Research Laboratory, USAF Academy, Colorado Springs, CO.

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